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Comments about the causes of deviations from the Anderson–Schulz–Flory distribution of the Fischer–Tropsch reaction products

I. Puskas[a,*,1], R.S. Hurlbut[b]

[a] *Amoco Chemical Company (now BP plc), Naperville, IL, 60566, USA*
[b] *Illinois Math and Science Academy, 1500 W Sullivan Rd, Aurora, IL 60506, USA*

Abstract

The purpose of this communication is to challenge the “evidence” for higher olefin incorporation into the Fischer–Tropsch (FT) products in secondary reactions and dispute the claims that these postulated reactions are responsible for the “positive deviations” from the Anderson–Schulz–Flory (ASF) distributions. Furthermore, arguments and information are presented to show that multiplicity of the chain growth probability is the only reasonable cause of the reported “positive deviations” in the C_{6+} product range.

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1. Historical background

Few subjects have attracted so much scientific interest during its 80 year history, than the Fischer–Tropsch (FT) synthesis of hydrocarbons from carbon monoxide and hydrogen. Within this subject, analyzing the products and defining the rules of product distributions have offered fascinating and challenging opportunities for numerous researchers. Below we shall present a brief review on this subject which, by necessity, is severely restricted by our judgement with respect to relevance and significance to our objectives. Furthermore, we consider only hydrocarbons (olefins and paraffins lumped together, ignoring isomeric differences) for our analyses, and ignore the formations of minor oxygenated synthesis products. Publications by Herington [1], Anderson and co-workers [2], Pichler and co-worker [3,4] provided a basic understanding of the reaction. Reviews by Henrici-Olive and Olive [5] showed that the reaction is a step-growth polymerization originally described mathematically by Schulz [6] and also by Flory [7]. The equations derived by Herington [1] and by Anderson [2] are essentially identical to that of Schulz; the Flory equation is not quite equivalent. The products can be described by a single parameter, the chain growth probability or growth factor or α:

$$W_n = (\ln^2\alpha) n\alpha^n$$

where W_n is the weight fraction of the products with n carbon number and α the chain growth probability or growth factor. The logarithmic form of this kinetic

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[*] Corresponding author. Present address: 939 Brighton Drive, Wheaton, IL 60187, USA. Tel.: +1-630-653-4897.
E-mail addresses: i.puskas@worldnet.att.net (I. Puskas), rshurl@imsa.edu (R.S. Hurlbut).
[1] Retired.

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expression is shown below:

$$\log \mathrm{C}_n = \log(\ln^2\alpha) + n \log \alpha$$

where $\mathrm{C}_n = W_n/n =$ mole fraction (more precisely, carbon selectivity fraction to eliminate the weight differences between olefins and the secondary product paraffins). According to the equation, a plot of $\log \mathrm{C}_n$ versus n should give a straight line (ASF plot).

However, in practice, “ideal” molecular weight distributions were never observed. The majority of the reported ASF plots showed a nearly straight line only in the C_4–C_{12} region. This made the experimental determination of α somewhat arbitrary. Most authors define the growth factor from the straight-line portion of the “ASF plot”. Schulz and co-workers [3] regularly report the growth factor for each individual carbon growth step.

Early work has established, that the ASF plots deviate from the predicted values in the C_1–C_3 range [5]. The methane is usually more than predicted, particularly over Co and Ru catalysts. This was attributed to hydrogenolytic cleavage of the 1-olefins in secondary reactions. Over Ru and Co catalysts, the C_2 and C_3 products are much less than predicted, while over Fe only slightly less. This finding is attributed to another secondary reaction of the olefins, namely incorporation into the polymer by initiating a new chain. Although evidence is lacking that the C_2 and C_3 products initially form in the amounts predicted by the ASF rules, this assumption is supported by the knowledge that ethene and propene polymerize at a fast rate to FT products over Co catalyst in the presence of H_2, even in the absence of CO [8,9]. Assuming that the C_2 and C_3 olefins initially form in the amount predicted by the ASF rules, we measured nearly identical extent of “depletion” of these olefins caused by incorporation into the polymer [10]. This suggests that the rate ratios of the olefin-initiated polymerization and of the polymerization by CO hydrogenation are essentially constant. Furthermore, due to fine refinements in the quantitative aspects of our analyses, we were able to show [10] that not only ethene and propene, but also butene and to a very small extent even pentene incorporate. In our treatment we assumed, that these olefins react with the CO-derived “carbon pool” (hence called the reaction telomerization), although olefin homopolymerization or copolymerization with the carbon pool cannot be ruled out.

Numerous papers reported deviations from the ideal ASF distributions outside the C_1–C_5 product range. Review articles [11–13] provide more details and possible explanations for the deviations. Considering the extreme difficulties in achieving controlled experimentation and accurate quantitative analyses of the products ranging from gases to waxes, it would not be surprising if some of the reported deviations were caused by flaws in experimentation or analyses or non-representative product sampling. Thus, Dictor and Bell [14] have shown that gas phase sampling of the products from liquid phase reactors (catalyst slurried in a hydrocarbon liquid) may not be representative for the reaction because of transient holdup of higher molecular weight products in the oil phase. Dictor and Bell also suggested that the same reasoning may also apply to vapor phase fixed bed reactors. According to our experience, GC sample injection can also be a potential source of error. For example, heavy products may not evaporate completely at the temperature of the injection port. Condensations in the heated sample lines in automated systems may cause non-representative sampling. Reaction conditions atypical for FT, e.g. testing a novel catalyst, may result in unexpected and unidentified reactions beyond CO hydrogenation, causing apparent deviations from the ASF distribution. Thus, caution may be advised to interpret the results from zeolite-supported FT catalysts in term of ASF distributions, because the zeolites themselves are known catalysts for hydrocarbon reactions.

A paper by Snel [15, and references therein] leads to reports about “negative” deviations. In these cases, the heavier products fall below the straight line of the ASF plot. In our studies [10] we have also observed “negative” deviations. However, we were unable to verify, whether the deviations were real or the result of analytical or sampling inadequacies. In light of the limited number of reports on negative deviations, and in light of the report by Dictor and Bell [14] that non-representative sampling may cause the observation of “negative deviations”, the case of “negative” deviations cannot be regarded as firmly established.

Experimental conditions resulting in selective hydrocracking of the high molecular weight products could possibly cause the observation of “negative deviations”.

In contrast, “positive” deviations characterized by concave curvatures in the ASF plots, or by a “break” in the C_{10}–C_{13} range, have been firmly established and extensively studied. Working with Fe catalysts in a fixed bed reactor, Koenig and Gaube [16] have found, that without alkali promotion, Fe gave ideal ASF distribution with low (0.65) value of growth probability. With K-promoted Fe, the product distribution gave curved ASF plot. These authors assumed that alkalization of the catalyst created two different catalytic sites with differing chain growth characteristics. The unpromoted sites produced low α-value, the alkalized sites gave high α-value. Based on this concept, they developed a mathematical model (“two-site model” or two superimposed ASF distributions) and calculated that 61% of the product was produced on unalkalized sites with 0.57α, and 39% on alkalized sites with 0.87α. As an alternative to the two-site model, a “distributed site” model was suggested by Stenger [17] and shown to be equivalent. The assumptions of this latter model are, that the K at the Fe sites is randomly distributed with concentrations between zero and a maximum value. Studying alkalized Fe catalysts in continuous stirred tank (slurry) reactors (CSTR), Satterfield and Huff [18] first reported ideal ASF distributions for the products. However, re-examinations with improved analytical accounting resulted in non-ideal product distributions which could be described by the two-site model, with 0.6–0.7 range for α_1 and 0.89–0.93 for α_2 [19,20]. Numerous other workers also reported similar findings with alkalized Fe from CSTRs. Non-ideal distributions requiring two α’s were also reported in a CSTR reactor over unpromoted Fe [21]. However, in this case, α_1 and α_2 differed much less (0.53 and 0.66, respectively).

Non-ideal product distributions were also observed on Ru catalysts in fixed bed experiments by Iglesia et al. [22]. These authors proposed that transport-enhanced heavy olefin readsorption and incorporation into the products via chain initiation is responsible for the findings. According to their scheme, hydrogenation of the olefins is inhibited by water (a product of the reaction) and the termination probability of the heavy olefins approaches zero. Hence the product molecular weight increases with increasing bed residence time. A mathematical model was developed which was claimed to account for the results quantitatively. The idea of heavy olefin incorporation originated from early work of Schulz et al. [23]. Co-feeding ^{14}C-labeled *n*-hexadecene-1 with $2H_2$–CO into a fixed bed reactor charged with Co-catalyst, 99.8% of the hexadecene converted. The products were hexadecane (79.4%), methane and other degradation products (14.1%) and incorporation into products with increased carbon number (6.3%). Schulz and Claeys [24] have continued their studies on the secondary reactions of the olefinic products and recently reported data on the reactivity of co-fed olefins from experiments carried out under pressure in CSTR with Co–Ru and Co–Re catalysts. They have also developed a kinetic model to account for the product distributions [25]. In concept, the model is analogous to that of Iglesia et al. [22], but developed for CSTR conditions and more focused on the secondary reactions of olefins. Furthermore, the basic assumptions concerning the enhanced readsorption of the primary olefins differ. Schulz has attributed it to olefin solubilities in the slurry liquids rather than enhanced adsorption due to diffusional limitations postulated by Iglesia et al. for the fixed bed experiments.

Sarup and Woiciekowski [26] reported both ideal and non-ideal product distributions over Co from experiments in stirred gas–solid reactor (SGSR) (Berty spinning basket reactor). These authors accounted for the non-ideal distributions by “two-location mechanism”, using two α’s. We previously reported [27] on our studies over Co catalysts in a fixed bed reactor at 103–241 kPa. We had a completely automated analytical system and generated a wealth of data on conversions, selectivities, growth factor and material balances. We derived the value of the growth factor from the C_6–C_{10} data, and the material balance values by analyses up to C_{10} and by calculation of the C_{11+} data assuming ideal ASF distributions in the heavy product range. The expected material balance value should be around 99.0–99.5% due to the formation of some oxygenates which were not analyzed for routinely. The range of measured growth factors was 0.66–0.82. The material balance values can be considered as indicators of the validity of the ASF scheme. Incomplete material balances mean positive deviations; excessive balances negative deviations. Considering the precision range associated with the manipulations, calibrations, calculation methods and lack of routine analyses for oxygenates (which can escalate under certain conditions [28]), material balances in the 95–103% range are considered as indicating ideal or nearly ideal ASF distributions. The measured range was 77.0–102.6%, with most of the data in the 91.0–102.6% range. The lowest material balance values were obtained from experimental conditions resulting in the highest measured α-values. In summary, the majority of our material balance measurements have indicated ideal or near ideal ASF distributions, another significant fraction indicated relatively small "positive" deviations and a few measurements strong "positive" deviations. Our data did not give indication of "negative" deviations. We have proposed that a multiplicity of the chain growth probability can account for the findings, and demonstrated this possibility by modeling studies.

As olefin incorporation became the suspected cause of the deviations from the ASF distribution, more olefin co-feeding studies were reported. These studies were extended to co-feeding of oxygenated compounds (alcohols etc.), because oxygenates are known to form in significant quantities over alkalized iron. Tau et al. [29,30] have shown that isotopically labeled ethanol and pentanol incorporate. On the basis of the radioactivity distribution, these authors proposed the existence of two chain growth mechanisms. They have also reported, that alcohols were not significant intermediates in their studies.

In light of the report [21], that unpromoted Fe can also give non-ideal product distributions requiring two α's for adequate description, Gaube and coworkers [31,32] have changed the basic assumptions of their kinetic model. Instead of the "two-site concept" associated with alkali promotion, it was postulated that two chain growth mechanisms exist with different chain growth probabilities. However, these changes in basic assumptions did not essentially change their model and its usefulness. These authors have also conducted co-feeding studies with higher 1-alkenes in a plug-flow reactor over Co, and disputed the claims that heavy olefin incorporation is significant and causes an increase of the chain growth probability in the heavy product range over Co catalysts. However, the same authors [32] have accepted the heavy olefin incorporation theories of Iglesia et al. [22] over Ru catalyst.

While the above reviewed deviations from the ASF kinetics are all accounted for by kinetic models based on a variety of assumptions, the fact is, that the reasons for the deviations are not known and still disputed. Furthermore, we came to entirely different conclusions concerning the causes of the deviations in fixed bed reactors over Co [27]. The continuing controversy on the subject prompted us to expand on the concept that a multiplicity of growth factors is always produced and that this sometimes results in measurable deviations from the ideal ASF distribution. Furthermore, we have developed arguments against the reported "evidences" of heavy olefin incorporation.

2. Argumentation for creation of a multiplicity of growth factors: consequences of the chain growth multiplicity with regard to the observed molecular weight distribution

Let us start with two basic assumptions:

1. Ideal ASF distribution with a single chain growth probability can be obtained only if the kinetic parameters (temperature, H_2/CO ratio, partial pressures of the individual reagents and inerts including reaction products) can be kept identical and constant in the immediate proximities of all catalytic sites throughout the reactor via a dynamic steady state equilibrium.
2. In heterogeneous catalytic reactions, like the FT synthesis, these conditions cannot be met. The basic reason for this is that the rates of reagent chemisorption from the immediate proximity of the catalytic sites—where long range molecular forces between the catalytic site and the gas molecules set in—are much faster than the rates of supply by transport, even in agitated systems. We emphasize, that the above sentences express assumptions and not statements. At this stage, proof by our own data or by literature reports is lacking. The reagent supply to the individual catalytic sites will be a function of the geometry of the reactor and the rates of gas transport and can be particularly restrained in granular or pelleted catalysts. The catalytic sites first in contact with the feed reduce the reagent concentration by chemisorption and also by dilution with reaction products. Catalytic sites with higher concentration of reagents give faster rate, generate more heat and produce more "diluents" for the feed stream. Consequently, the steady state conditions established for the immediate surroundings

of the individual catalytic sites will differ throughout the reactor. The different kinetic parameters in the different microscopic environments lead to infinite number of chain growth probabilities.

Literature reports indicate that the value of the growth factor decreases with increasing temperature, increasing H_2/CO ratio, increasing hydrogen partial pressure and decreasing carbon monoxide partial pressure. Studying the response of the growth factor to changes in the experimental variables over Co in a fixed bed reactor [27], we came to analogous conclusions. In addition, we have also demonstrated, that adding inerts to the feed (i.e. decreasing the partial pressure of the reagents) also results in lower α-value. This summarizes our knowledge on the influence of kinetic parameters on the growth factor. Furthermore, attention is called to the difficulties in measuring and controlling the surface temperatures. Matyi et al. [33] have measured the internal magnetic field of iron carbide crystallites by Moessbauer spectroscopy before and during simulated FT reaction conditions. Since the internal magnetic field is temperature dependent, they were able to calculate the temperature on the catalyst surface. This was found to be 13–19 K higher than the bulk catalyst temperature. The paper [33] also gives references considering the subject. Most of the cited studies estimated nearly an order of magnitude higher local temperature rises than the reported 13–19 K range, but one study suggested only less than 0.03% temperature difference.

With this limited knowledge about the factors influencing the value of the chain growth probability, we try to evaluate our expectations in the types of reactors most commonly used in research laboratories. Let us consider first the plug-flow reactor (PFR), which is usually operated in the downflow mode. Since reagents preferentially chemisorb from flowing gas mixture, the top of the reactor will give higher reagent concentrations on the catalyst surface, hence higher rate. Normally this should also result in higher α-value. In practice, because of difficulties with heat removal, plug-flow reactors usually develop some degree of temperature gradient along the axes, often resulting in “hot spots”. In our work [10,27] thermal control appeared satisfactory due to favorable reactor design, the use of nitrogen-diluted feed, and the use of catalyst particles with low Co content. We measured usually 0.7–2.2 K higher temperature in thermowell location at the upper part of the bed. We do not know how this translates to true temperature differences between the individual catalytic sites; it may easily be in the 10–30 K range. While temperature profiles are well known to occur in commercial plug-flow reactors [34], laboratory studies may not have paid sufficient attention to this phenomenon. Based on purely reagent concentration profile, the growth factor should decrease with increasing bed length. Due to the “undocumented” temperature profiles (hot spots), lower α may be produced at the top of the reactor. In short, a multiplicity of growth factors are expected, An additional increase in the range of the growth factor may occur, if the feed composition does not correspond to the H_2/CO usage ratio, or if the catalyst has water-gas shift activity. In these instances, the H_2/CO ratio changes with the length of the catalyst bed.

We also checked the literature concerning chain growth probability in plug-flow reactors. Rice and Wojciechowski [35] rightfully questioned the kinetic values of data generated in plug-flow reactors. However, their theoretical treatment did not consider temperature profiles and dilution effects, apparently because information on this subject was not available at the time of their work. Three studies were found on the dependence of chain growth on the bed-length in PFR. Everson and Mulder [36] reported increasing product molecular weight with increasing bed length over Ru. These findings seem to be in agreement with the postulation of Iglesia et al. [22] that the molecular weight increases with increasing contact time. Everson and Moulder also reported increasing product molecular weights with increasing temperature. This finding is unprecedented and hence definitely controversial. We advanced a plausible explanation to these findings. We believe, that on the top of the reactor, due to hot spot, low molecular weight products were generated. As the reactor bed length was increased, the fraction of the low molecular weight products became smaller with increasing conversion. A further significant aid to chain growth must have been provided by a decrease of H_2/CO ratio along the vertical axis. Their feed had 1.86 initial H_2/CO ratio. Due to the known high usage ratio over Ru (>2.1), the H_2/CO ratio must have declined sharply with increasing bed length. Similar arguments can be advanced to explain the controversial temperature effects. On top of the reactor, hot spots developed irrespective of the reactor temperature. At higher temperature, due to higher conversions, the H_2/CO ratio must have dropped to a level favoring very high molecular weight products even at the higher reactor temperature. Darby and Kemball [37] found no variations in the products with bed length over Co. Feimer et al. [38] reported that, over promoted Fe, the product distribution is independent of reactor length, except at high CO conversions. However, questions may be raised about the validity of the conclusions of both Darby and Kemball and Feimer et al. In both papers, the conclusions were based on gas sample analyses for products up to C_6. Our modeling studies (see Figs. 1–3) have demonstrated, that minor changes in growth factor assumptions cause relatively small changes in the product mole fractions, which may not be easily distinguishable analytically.

We suggest, that not even the SGSR can provide identical microscopic steady state conditions for the individual catalytic site environments. Intra-pellet diffusion limitations cannot be overcome by agitation. A narrower range of growth factor is expected. In agreement with these expectations, reports were found of ASF plots from SGSR showing approximately strait lines or showing a “break” [26].

We proceed now to discuss our expectations in CSTR. The literature review revealed that the broadest α-ranges were obtained over alkalized Fe catalysts in CSTR. While the two-site model or mechanism-based two α-model could possibly account for broadening of the molecular weight distribution upon alkalization of Fe, it is less clear how olefin incorporation could be responsible for it. We have developed an alternative hypothesis, which, we believe, may give the most rational explanation for the experimental findings. In CSTR, the feed is introduced to the bottom of the liquid reaction medium as tiny vapor phase bubbles. Some of the reagents may dissolve in the

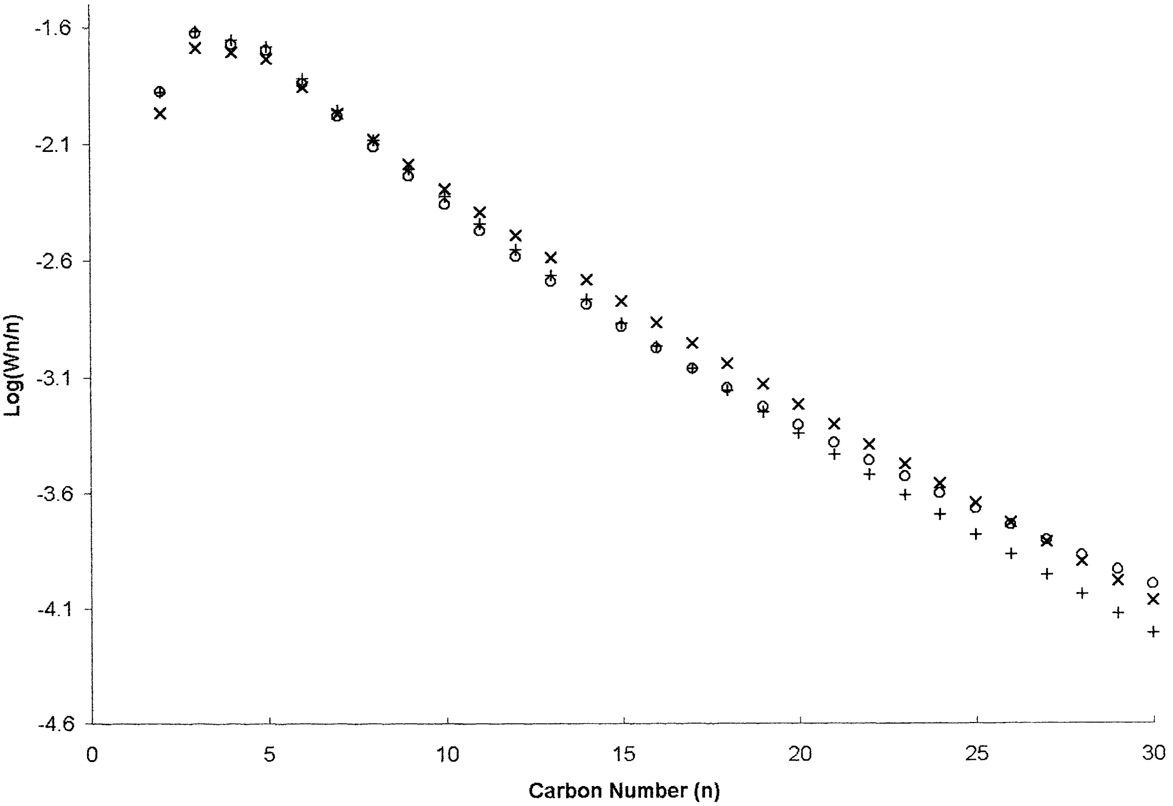

Fig. 1. Calculated ASF plots: (○) continuously changing growth factors from 0.60 to 0.90; (+) distribution from $\alpha_1 = 0.675$ (50%) and $\alpha_2 = 0.825$ (50%); (×) distribution from $\alpha_1 = 0.675$ (30%) and $\alpha_2 = 0.825$ (70%).

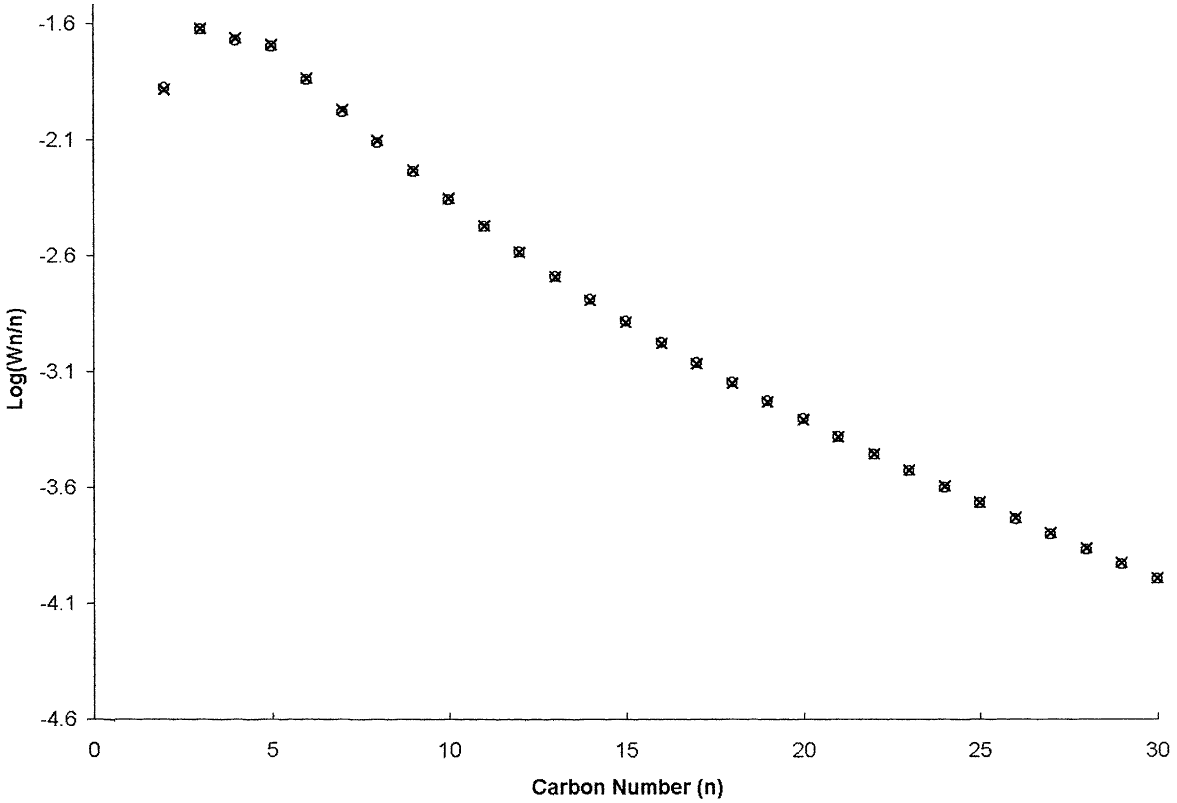

Fig. 2. Comparison of calculated ASF plots: (○) continuously changing growth factors from 0.60 to 0.90; (×) best fit two α's ($\alpha_1 = 0.693$ 65%; $\alpha_2 = 0.866$, 35%).

liquid medium, but the bulk of the reagent transport is provided by the bubbles. The bubbles may be temporarily attached to the slurried catalyst particles or may become contacted with them. During these brief periods, reagent adsorption, reaction, product desorption occur in fast sequence. Since desorption quickly changes the composition of the bubbles, the product distribution will change during the short periods of attachment or contact. Agitation will not prevent these changes, since the catalyst particles and the bubbles travel with the agitation. The changes in product distribution are particularly great with alkalized Fe catalyst. While alkali promotion is known to lead to considerably higher α-value, it also results in strong water-gas shift activity, and hence in rapid changes in the H_2/CO ratios in the individual bubbles. This, in turn, causes an excessive broadening of α-range. Two α's were required to describe the molecular weight distributions. From the report of Stenger [17] it is known that the two-site model and the distributed site model are equivalent in the sense that, mathematically, both can define the observed molecular weight distributions. Our proposed scheme of "multiplicity model" [27] is similar to the "distributed site" model with respect to the continuously changing range of α, but it differs in basic concepts and assumptions.

The arguments described above should be convincing that in FT syntheses a multiplicity of α's is produced, even though two α's may suffice to define the distributions satisfactorily. In our cited paper [27], we have already provided examples of calculated molecular weight distributions assuming continuously changing α's within a limited range. Our "telomerization model" developed for Co-catalyzed FT products, which considers C_2–C_4 olefin incorporation [10], was used for the calculations. These calculations have demonstrated, that if the range of the assumed α's is narrow, a single α can adequately describe the

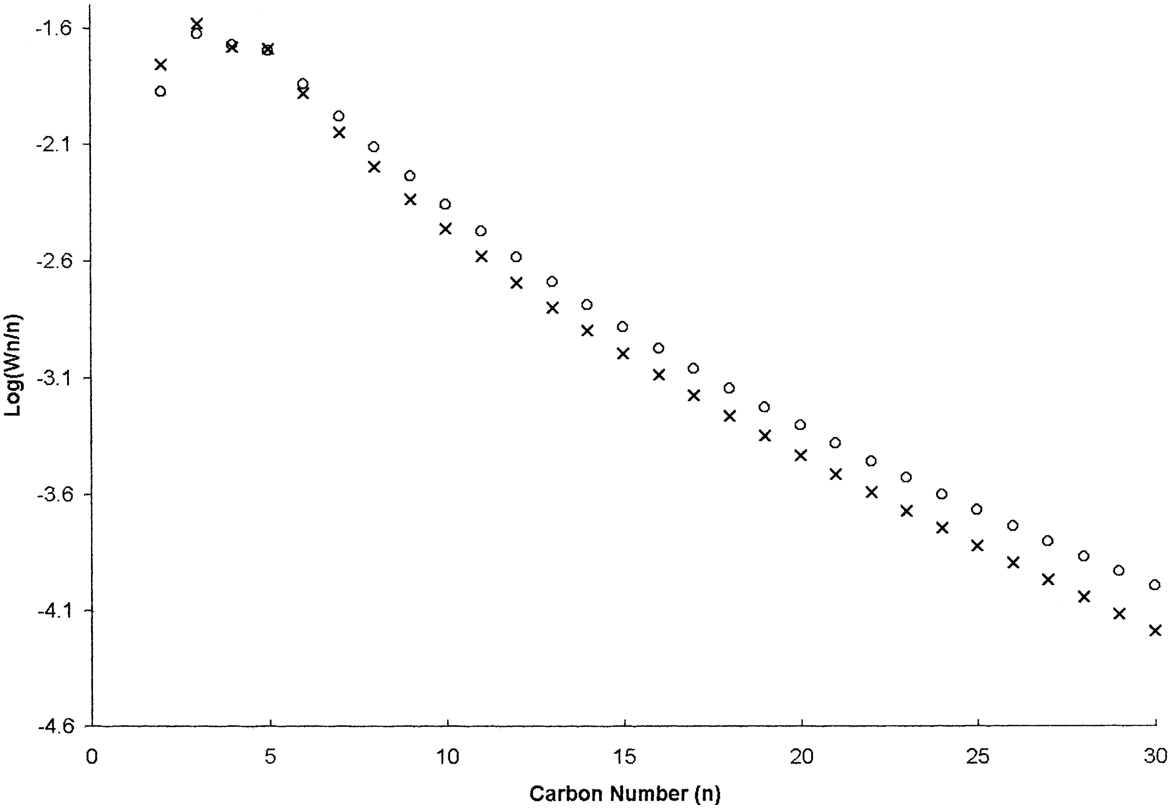

Fig. 3. ASF plot generated with three α-assumption: ($\times$) distribution from $\alpha_1 = 0.45$ (30%), $\alpha_2 = 0.70$ (40%), and $\alpha_3 = 0.85$ (30%); ($\circ$) continuously changing growth factors from 0.60 to 0.90.

molecular weight distribution. The deviations from an ideal ASF distribution are so little, that they cannot be convincingly detected with available analytical accuracies. If the assumed α-ranges were wide, the calculated ASF plots showed smooth curving "positive deviations", exhibiting increasing curvature with increasing assumed α-ranges. Additional examples are shown in Fig. 1. Here calculated distributions are compared from three different assumptions. In the base case (symbol '$\circ$'), α continuously changes between 0.60 and 0.90. In the second case (symbol '+'), two single α's were selected (0.675 and 0.825) in 50–50% proportions. Note that these α's are at the one- and three-quarter points of the range of the first assumption. The agreement with the continuous α-plot is good in the lower carbon number range, but less satisfactory in the higher carbon number range. In the third case (symbol '$\times$'), the same two α's were selected as previously, but in 30–70% proportions, respectively. This gave a less satisfactory agreement with the continuous α-plot in the middle-carbon range. A notable and expected difference is the smaller curvature with the two α-assumption. The two α's and their fractions, which provide the best fit to the continuous distribution with 0.6–0.9 α-range, were calculated by regression analyses as 0.693 (65%) and 0.866 (35%). As Fig. 2 illustrates, the distributions calculated with the continuous model and the best fit two α-model are essentially identical.

In our continuous α-assumptions, we assumed even changes of α within the specified range. In reality, on the basis of our argument, this cannot be expected to be true. Here it becomes convenient to use two α's to describe the molecular weight distribution. A broad range of α's with uneven continuous changes can be divided into two narrower ranges, each reasonably represented by a single α due to the narrowness of the range. Very broad and very uneven continuous distributions may even require three α's for adequate representation. In Fig. 3, we show an ASF plot generated with a three α-assumption ($\alpha_1 = 0.45$, 30%; $\alpha_2 = 0.70$, 40%; $\alpha_3 = 0.85$, 30%). For comparison, the plot with continuous α-assumption between 0.60 and 0.90 limits is also shown in Fig. 3. All the plots in the figures show concave curvatures and a "break" from the straight line to slight curving in the C_{10}–C_{14} range. Our model could not generate ASF plots similar to those reported by Bukur et al. [39], when a "bump" appeared on a curving ASF plot. Neither can generate negative deviations by our model.

3. The extent of olefin incorporation and its influence on the molecular weight distribution: challenging the heavy olefin incorporation theories

The incorporation of lower olefins by new chain initiation has been well established and considered to be responsible for the low C_2–C_4 content in the ASF plot [5,10]. Our model has suggested [10] that incorporation of the lower olefins causes a small parallel shift in the ASF plot, without affecting the value of the growth factor. The incorporation of C_2–C_4 olefins into the FT products was confirmed by numerous co-feeding studies including labeled species [3,40,41 and references therein]. Reviewing these studies, none of them suggested, that lower olefin incorporation would cause "positive deviations" in the high molecular weight region of the ASF plots.

Massive incorporation of the heavier olefins by chain initiation and subsequent "regular" propagation, in principle, could create increasing growth factors for the heavier products, resulting in "positive deviations". The "regular" propagation means that the olefin-initiated chain has the same growth factor as the CO-initiated chain. Concerning heavy olefin incorporation over Co, the best evidence is the already mentioned radioactive tracer work of Schulz et al. [23] carried out in a plug-flow reactor with n-hexadecene-1 co-feeding. Initiation of a chain at the C_{16} level, with the same growth factor as the CO-derived chain, should result in equal molar radioactivity in all C_{17+} products. The C_{17}–C_{20} products had approximately equal molar radioactivity. The molar radioactivity declined at C_{21}. Unfortunately, analyses were not reported for higher number products. Thus, this experiment does not provide satisfactory information about a possible increase in the growth factor. The tracer work also indicated that 14.1% of the hexadecene degraded to methane and C_{16-} hydrocarbons. Thus, an overall molecular weight increase is less likely even if the chain initiation at C_{16} would result in "regular" growth. Furthermore, it must be realized, co-feeding hexadecene-1 with synthesis gas provided a much more favorable kinetic environment for hexadecene incorporation, than regular synthesis conditions without the co-feed.

In another attempt to incorporate olefins, Schulz and Claeys [24] co-fed C_2–C_{11} olefins with synthesis gas into a CSTR under high pressure with slurried CoRu or CoRe catalysts. The authors reported that ethene was very reactive, propene was the least reactive olefin; and with increasing carbon number, the olefin reactivity increased exceeding that of ethene at about C_9. However, these results should be viewed with caution. They may be misleading, because they do not consider the exponentially increasing residence times for the higher boiling olefins in the high pressure slurry reactor. Reactor effluent analyses provided measurements of the extent of hydrogenation, isomerization and hydroformylation of the co-fed olefins. The missing balance was attributed to olefin incorporation, sometimes exceeding 40%. The conclusions based on the missing material balance may be questionable, because hold-up in the liquid phase reactor may have resulted in non-representative gas phase samples used for the analyses [14]. This argument seems to be supported by the finding, that the missing balance was the highest at high pressures. Furthermore, the possibility was not considered that the higher olefins or the corresponding hydrogenated products may have degraded, hydrogenolyzed during their extremely long residence time. Hence the values derived for olefin incorporation, based on missing material balance, cannot be relied upon with certainty. An examination of the plots in this same paper [24] reveals more about olefin incorporation. From the ethene and octene co-feeding experiments, the expectation is a parallel shift compared to the base case, if the growth factor of the olefin-initiated chain were identical to that of the regular chain. Fig. 8 of the paper does not provide a clear picture. Ethene incorporation appeared to show a definite parallel shift for the C_3–C_{10} range, but then the shift disappeared. Octene incorporation appeared to cause only a slight parallel shift comprising three or four carbon atoms, but at higher C-levels the shift disappeared. Thus, this comparison does not provide a clear picture either, though it shows a much greater extent of ethene incorporation. More significant and relevant information can be gained from Fig. 2 of the paper showing the chain growth probabilities for the base case measurements. Four out of the six graphs show essentially identical growth factors for the C_6–C_{14} range, indicating "ideal" ASF conditions in this range. If olefin incorporation occurred at each C_n-level via new chain initiation, with increasing olefin reactivity with growing C-number, the growth factor at each C_{n+1} level should be increasingly greater, ultimately resulting in a concave curvature. Two of the graphs show some initial growth factor increases, but later convex curvatures were indicated. Based on these findings, we do not see evidence for heavier olefin incorporation. Undeniably, the tracer studies have indicated the possibility of some heavy olefin incorporation, but evidence is lacking that this impacts the molecular weight distribution and the value of the chain growth probability.

It is interesting to note, that regarding co-feeding hexene-1 or octene-1 with synthesis gas to Co-catalyst in a PFR, Gaube et al. [32] made similar observations, as Schulz and Claeys [24]. In both cases, olefin incorporation appeared to be limited to a few carbon growth. Thus, there is doubt that the longer chain, olefin-initiated chain, can grow with the same growth factor as the CO-derived chain. It appears, that the growth of longer chain olefins is limited to a few carbon atoms. A plausible explanation to this tentative conclusion may be that the added olefins adsorb on "islands" surrounded by carbon pools, since growth requires relatively long migration of the CH_2 intermediates, growth may be limited to the periphery of the "islands".

The best-appearing experimental evidence for heavy olefin incorporation over Ru catalyst reported by Iglesia et al. [22,42] was based on residence time studies in a plug-flow reactor. We wish to propose an alternative interpretation of the ASF plot presented in Fig. 2 of Ref. [22] and in Fig. 5 of Ref. [40]. The heavy products (C_{22}–C_{49}) indicate essentially parallel shift curved lines for the 2.0–2.5 and 12 s contact times, respectively. The curved lines indicate non-ideal ASF distributions. The apparent parallelism mathematically means numerically identical growth probabilities for the individual growth steps in this carbon range. This seems to suggest that the residence time did not affect the growth probabilities of the heavy products. The parallel shift is due to larger mole fraction of lighter product formation at 2.0–2.5 s residence time, resulting in lower mole fractions of heavy product formation, but this does not affect the values of the growth factor in the heavy range. We suggest that a hot spot may have occurred on the top of the reactor causing the formation of lighter products. In a previous publication [27] we have shown, that, in PFR, higher space velocity increases catalyst productivity (rate) probably because of faster reagent diffusion to the catalyst. Increased rate, in turn, may lead to local overheating (hot spots). Although the authors reported temperature control within 0.5 K, it is possible that the location of their thermocouple did not allow the detection of the hot spot. As discussed above, hot spots always form in plug-flow reactors. In fact, in experiments with Fe catalysts, using the same reactors as in the work under discussion, Madon and Taylor [43] reported 5–25 K higher hot spot temperatures near the top of the reactor.

4. Summary

The Schulz and Flory equations were originally developed to describe the products of step-growth polymerization by a single parameter, α. When applied to FT products, experimental data deviated from the distributions predicted by the equation. Based on a review of the literature, and on our experimental and modeling work, we conclude, that the equations are fundamentally correct and the deviations can be almost quantitatively accounted for by kinetic considerations and by accounting for the various secondary reactions. Kinetically, the equation is valid only, if the microscopic kinetic environment can be kept identical and constant at each catalytic site of the synthesis. It is proposed, that these conditions cannot be achieved, and for this reason, a multiplicity of growth factors is produced. If the range of the growth factors is narrow, a single α may suffice to adequately describe the product distribution. If the range of the growth factors is broad, the ASF plots show concave curvatures instead of straight lines. In these instances, the product distributions can be mathematically defined by two “imaginary” α’s and associated “imaginary” product proportions. Additional observed deviations from the ASF plots are caused by the secondary reactions of the olefinic products. Of these, the incorporation of the C_2–C_4 olefins into the chain is well established. The hydrogenolytic cleavage of the olefins can cause excessive methane formation. Other secondary reactions probably also occur, but these do not seem to cause observable impact on the molecular weight distributions under usual FT reaction conditions.

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